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(54) Title: CLEANSING COMPOSITIONS

(57) Abstract

A personal cleansing product comprising: (a) from about 5 % to about 50 % by weight of a mixed surfactant system which comprises: (i) from about 1 % to about 20 % by weight of composition of anionic surfactant, and (ii) from about 1 % to about 20 % by weight of composition of amphoteric surfactant, (b) from about 3 % to about 40 % by weight of an insoluble nonionic oil or wax, and (c) water, wherein the anionic surfactant and amphoteric surfactant together comprises from about 5 % to about 30 % by weight of the composition, the weight ratio of anionic surfactant:amphoteric surfactant is in the range from about 1:5 to about 20:1, the weight ratio of total surfactant:nonionic oil or wax is in the range from about 10:1 to about 1:3, and wherein the composition is in the form of an oil-in-water emulsion having a viscosity in the range from 10,000 to 40,000 cps and a yield point of at least 50 dyne/cm². The cleaning products demonstrate excellent lathering, mildness, stability, rinsability and conditioning benefits.

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CLEANSING COMPOSITIONS TECHNICAL FIELD

The present invention relates to cleansing compositions. In particular it relates to foam-producing personal cleansing compositions suitable for simultaneously cleansing and conditioning the skin and/or the hair and which may be used, for example, in the form of foam bath preparations, shower products, skin cleansers, hand, face and body cleansers, shampoos, etc.

BACKGROUND OF THE INVENTION

Foaming cosmetic compositions must satisfy a number of criteria including cleansing power, foaming properties and mildness/low irritancy with respect to the skin, hair and the ocular mucosae. Skin is made up of several layers of cells which coat and protect the keratin and collagen fibrous proteins that form the skeleton of its structure. The outermost of these layers, referred to as the stratum corneum, is known to be composed of 250 Å protein bundles surrounded by 80 Å thick layers. Hair similarly has a protective outer coating enclosing the hair fibre which is called the cuticle. Anionic surfactants can penetrate the stratum corneum membrane and the cuticle and, by delipidization destroy membrane integrity. This interference with skin and hair protective membranes can lead to a rough skin feel and eye irritation and may eventually permit the surfactant to interact with the keratin and hair proteins creating irritation and loss of barrier and water retention functions.

Ideal cosmetic cleansers should cleanse the skin or hair gently, without defatting and/or drying the hair and skin and without irritating the ocular mucosae or leaving skin taut after frequent use. Most lathering soaps, shower and bath products, shampoos and bars fail in this respect.

Certain synthetic surfactants are known to be mild. However, a major drawback of most mild synthetic surfactant systems when formulated for shampooing or personal cleansing is poor lather performance compared to the highest shampoo and bar soap standards. Thus, surfactants that are among the mildest, such as sodium lauryl glyceryl ether sulfonate, (AGS), are marginal in lather. The use of known high sudsing anionic surfactants with lather boosters, on the other hand, can yield acceptable lather volume and quality but at the expense of clinical skin mildness. These two facts make the surfactant selection, the lather and mildness benefit formulation process a delicate balancing act.

Despite the many years of research that have been expended by the toiletries industry on personal cleansing, the broad mass of consumers remain dissatisfied by the mildness of present day cleansing compositions, finding, for example, that they have to apply a separate cosmetic lotion or cream moisturizer to the skin after using a shower or bath preparation in order to maintain skin suppleness and hydration and to counteract the delipidizing effect of the cleanser.

Thus a need exists for personal cleansing products which will produce a foam which is abundant, stable and of high quality, which are effective hair and skin cleansers, which will not dehydrate the skin or result in loss of skin suppleness, and which will provide a level of skin conditioning performance in a wash and rinse-off product which previously has only been provided by a separate post-cleansing cosmetic moisturizer, which has good rinsibility characteristics, and which at the same time has stable product and viscosity characteristics and remains fully stable under long term and stressed temperature storage conditions.

SUMMARY OF THE INVENTION

The subject of the present invention is a foam-producing cleansing product suitable for personal cleansing of the skin or hair and which may be used as foam bath and shower products, skin cleansers and shampoos etc. According to one aspect of the invention, there is provided a personal cleansing composition comprising:

- (a) from about 5% to about 50% by weight of a mixed surfactant system which comprises:
 - (i) from about 1% to about 20% by weight of composition of anionic surfactant, and
 - (ii) from about 1% to about 20% by weight of composition of amphoteric surfactant,
- (b) from about 3% to about 40% by weight of an insoluble, nonionic oil or wax or mixture of insoluble, nonionic oils or waxes, and
- (c) water,

wherein the anionic surfactant and amphoteric surfactant together comprise from about 5% to about 30% by weight of the composition, the weight ratio of anionic surfactant:amphoteric surfactant is in the range from about 1:5 to about 20:1, the weight ratio of total surfactant: nonionic oil or wax is in the range from about 10:1 to about 1:3, and wherein the composition is in the form of an oil-in-water emulsion having a viscosity (Brookfield RVT, Helipath, Spindle TB, 5 rmp, 25°C, 1min) in the range from 10,000 to 40,000 cps and a yield point of at least 50 dynes/cm² (Brookfield RVT, Spindle CP52, Plate Code A, 25°C).

All concentrations and ratios herein are by weight of the cleansing composition, unless otherwise specified. Surfactant chain lengths are also on a weight average chain length basis, unless otherwise specified.

The invention relates to a foam-producing cleansing composition with superior lathering characteristics (creaminess, abundance, stability) combined with excellent mildness to the skin and hair, together with good stability, cleansing ability and conditioning performance. The invention also relates to a wash and rinse-off personal cleansing product having the above lathering, mildness, rinsibility, stability and conditioning benefits.

The cleansing compositions herein are based on a combination of mild surfactants which in general terms can be selected from anionic, amphoteric, nonionic and betaine surfactants and mixtures thereof. The compositions preferably comprise a mixture of anionic and amphoteric surfactants and highly preferred systems also incorporate a nonionic or

betaine surfactant. Other suitable compositions within the scope of the invention comprise mixtures of anionic with one or more nonionic or betaine surfactants or mixture thereof; and mixtures of amphoteric with one or more nonionic or betaine surfactants or mixture thereof. The level of each of the anionic and amphoteric surfactants is generally in the range from about 1% to about 20%, preferably from about 2% to about 15%, and especially from about 3% to about 12% by weight of the composition. The weight ratio of anionic surfactant:amphoteric surfactant, on the other hand is generally from about 1:5 to about 20:1, preferably from about 1:2 to about 5:1, and especially from about 1:1 to about 2:1. The total level of anionic and amphoteric surfactants is generally about 5% to about 30%, preferably from about 8% to about 25% and especially from about 10% to about 20% by weight of the cleansing composition. The nonionic or betaine surfactant, on the other hand, preferably constitutes from about 0.1% to about 20%, more preferably from about 0.1% to about 10% and especially from about 1% to about 8% by weight of the composition. The total level of surfactant, inclusive of anionic, amphoteric, nonionic, betaine and other surfactant components, is preferably from about 5% to about 50%, more preferably from about 10% to about 30% by weight of composition.

Anionic surfactants suitable for inclusion in the compositions of the invention can generally be described as mild synthetic detergent surfactants and include ethoxylated alkyl sulfates, alkyl glyceryl ether sulfonates, methyl acyl taurates, fatty acyl glycines, N-acyl glutamates, acyl isethionates, alkyl sulfosuccinates, alpha-sulfonated fatty acids, their salts and/or their esters, alkyl phosphate esters, ethoxylated alkyl phosphate esters, acyl sarcosinates and fatty acid/protein condensates, and mixtures thereof. Alkyl and/or acyl chain lengths for these surfactants are C₈-C₂₂, preferably C₁₀-C₁₈.

Preferred for use herein from the viewpoint of optimum mildness and lathering characteristics are the salts of sulfuric acid esters of the reaction product of 1 mole of a higher fatty alcohol and from about 1 to about 12 moles of ethylene oxide, with sodium and magnesium being the preferred counterions. Particularly preferred are the alkyl sulfates containing from about 2 to 6, preferably 2 to 4 moles of ethylene oxide,

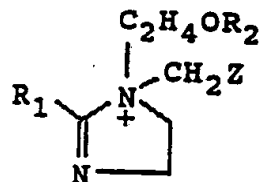
such as sodium laureth-2 sulfate, sodium laureth-3 sulfate and magnesium sodium laureth-3.6 sulfate. In preferred embodiments, the anionic surfactant contains at least about 50%, especially at least about 75% by weight of ethoxylated alkyl sulfate. Again, in preferred embodiments, the anionic surfactant counterions are selected from magnesium and mixtures of magnesium with one or more counterions selected from alkali metal, ammonium and alkanolammonium, this being preferred from the viewpoint of providing optimum lathering, mildness, emolliency, viscosity and stability. Thus, according to another aspect of the invention there is provided a personal cleansing composition comprising:

- (a) from about 5% to about 50% by weight of a mixed surfactant system which comprises:
 - (i) from about 1% to about 20% by weight of composition of anionic surfactant, and
 - (ii) from about 1% to about 20% by weight of composition of amphoteric surfactant,
- (b) from about 3% to about 40% by weight of an insoluble, nonionic oil or wax or mixture of insoluble, nonionic oils or waxes, and
- (c) water,

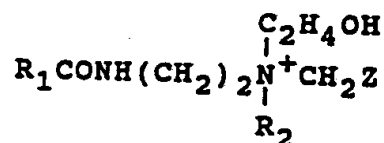
wherein the anionic surfactant and amphoteric surfactant together comprise from about 5% to about 30% by weight of the composition, the weight ratio of anionic surfactant:amphoteric surfactant is in the range from about 1:5 to about 20:1, the weight ratio of total surfactant: nonionic oil or wax is in the range from about 10:1 to about 1:3, and wherein the anionic surfactant counterions are selected from magnesium and mixtures of magnesium with one or more counterions selected from alkali metal, ammonium and alkanolammonium. In preferred embodiments, magnesium is preferably present in an amount equivalent to at least 10 mole %, preferably at least 20 mole % of the anionic surfactant. It will be understood that magnesium can be introduced into the compositions of the invention either as the preformed magnesium or partial magnesium salt of the anionic surfactant, or in the form of a water-soluble, non-surface active magnesium salt, for example magnesium chloride, magnesium sulfate or hydrate thereof.

Preferred compositions for use herein also contain an amphoteric surfactant. Amphoteric surfactants suitable for use in the compositions of the invention include:

- (a) imidazolinium surfactants of formula (II)



wherein R_1 is C7-C22 alkyl or alkenyl, R_2 is hydrogen or CH_2Z , each Z is independently CO_2M or CH_2CO_2M , and M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium; and/or ammonium derivatives of formula (III)

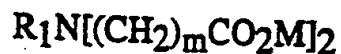


wherein R_1 , R_2 and Z are as defined above;

- (b) aminoalkanoates of formula (IV)



and iminodialkanoates of formula (V)



wherein n and m are numbers from 1 to 4, and R_1 and M are independently selected from the groups specified above; and

(c) mixtures thereof.

Suitable amphoteric surfactants of type (a) are marketed under the trade name Miranol and Empigen and are understood to comprise a complex mixture of species. Traditionally, the Miranols have been described as having the general formula II, although the CTFA Cosmetic Ingredient Dictionary, 4th Edition indicates the non-cyclic structure III. In practice, a complex mixture of cyclic and non-cyclic species is likely to exist and both definitions are given here for sake of completeness. Preferred for use herein, however, are the non-cyclic species.

Examples of suitable amphoteric surfactants of type (a) include compounds of formula II and/or III in which R_1 is C_8H_{17} (especially isocapryl), C_9H_{19} and $C_{11}H_{23}$ alkyl. Especially preferred are the compounds in which R_1 is C_9H_{19} , Z is CO_2M and R_2 is H; the compounds in which R_1 is $C_{11}H_{23}$, Z is CO_2M and R_2 is CH_2CO_2M ; and the compounds in which R_1 is $C_{11}H_{23}$, Z is CO_2M and R_2 is H.

In CTFA nomenclature, materials preferred for use in the present invention include cocoamphocarboxypropionate, cocoamphocarboxy propionic acid, and especially cocoamphoacetate and cocoamphodiaceate (otherwise referred to as cocoamphocarboxyglycinate). Specific commercial products include those sold under the trade names of Empigen CDL60 and CDR 60 (Albright & Wilson) Miranol H2M conc., Miranol C2M Conc. N.P., Miranol C2M Conc. O.P., Miranol C2M SF, Miranol CM Special (Rhone-Poulenc); Alkateric 2CIB (Alkaril Chemicals); Amphoterge W-2 (Lonza, Inc.); Monateric CDX-38, Monateric CSH-32 (Mona Industries); Rewoteric AM-2C (Rewo Chemical Group); and Schercotic MS-2 (Scher Chemicals).

It will be understood that a number of commercially-available amphoteric surfactants of this type are manufactured and sold in the form of electroneutral complexes with, for example, hydroxide counterions or with anionic sulfate or sulfonate surfactants, especially those of the sulfated C_8 - C_{18} alcohol, C_8 - C_{18} ethoxylated alcohol or C_8 - C_{18} acyl

glyceride types. Preferred from the viewpoint of mildness and product stability, however, are compositions which are essentially free of (non-ethoxylated) sulfated alcohol surfactants. Note also that the concentrations and weight ratios of the amphoteric surfactants are based herein on the uncomplexed forms of the surfactants, any anionic surfactant counterions being considered as part of the overall anionic surfactant component content.

Examples of suitable amphoteric surfactants of type (b) include salts, especially the triethanolammonium salts and salts of N-lauryl-beta-amino propionic acid and N-lauryl-imino-dipropionic acid. Such materials are sold under the trade name Deriphath by Henkel and Mirataine by Rhone-Poulenc. Amphoterics preferred for use herein, however, are those of formula II and/or III.

The compositions of the invention also contain from about 3% to about 40%, preferably from about 5% to about 20%, and more preferably from about 8% to about 15% by weight of an insoluble nonionic oil or wax or mixture thereof, the oil or wax being insoluble in the sense that it is insoluble in the cleansing composition liquid matrix at a temperature of 25°C. In addition, the oil or wax is present in composition in a level such that the weight ratio of total surfactant:oil or wax is in the range from about 10:1 to about 1:3,, preferably from about 5:1 to about 1:2, and especially from about 2:1 to about 1:1, this being preferred from the viewpoint of providing personal cleansing compositions having optimum lathering, mildness, emolliency, rinsibility and stability characteristics.

Suitable oils and waxes for use herein can be selected from water-insoluble silicones inclusive of non-volatile polyalkyl and polyaryl siloxane gums and fluids, volatile cyclic and linear polyalkylsiloxanes, polyalkoxylated silicones, amino and quaternary ammonium modified silicones, rigid cross-linked and reinforced silicones and mixtures thereof, C₁-C₂₄ esters of C₈-C₃₀ fatty acids such as isopropyl myristate and cetyl ricinoleate, beeswax, saturated and unsaturated fatty alcohols such as behenyl alcohol, hydrocarbons such as mineral oils, petrolatum and squalene, fatty sorbitan esters (see US-A-3988255, Seiden, issued October 26th 1976), lanolin and oil like lanolin derivatives, animal and

vegetable triglycerides such as almond oil, peanut oil, wheat germ oil, linseed oil, jojoba oil, oil of apricot pits, walnuts, palm nuts, pistachio nuts, sesame seeds, rapeseed, cade oil, corn oil, peach pit oil, poppyseed oil, pine oil, castor oil, soybean oil, avocado oil, safflower oil, coconut oil, hazlenut oil, olive oil, grapeseed oil, and sunflower seed oil, and C₁-C₂₄ esters of dimer and trimer acids such as diisopropyl dimerate, diisostearylmalate, diisostearyldimerate and triisostearyltrimerate. Of the above, highly preferred from the viewpoint of optimum lathering and mildness are the vegetable triglyceride oils.

Preferred from the viewpoint of conditioning effectiveness in a rinse-off application are compositions in the form of oil-in-water emulsions wherein the average size of the emulsion droplets is in the range from about 1 to about 150 microns, preferably from about 2 to about 50 microns, and more preferably from about 3 to about 10 microns (droplet size being measured by, for example, laser diffraction using, e.g. a Malvern Series 2600).

The oil or wax is preferably used herein in combination with a mild surfactant system. Suitable mild surfactants include those having a Relative Skin Barrier Penetration Value of less than about 75, preferably less than about 50 and more preferably less than about 40, Relative Skin Barrier Penetration Value being measured according to the test method set out in EP-A-0203750 (Incorporated herein by reference). Surfactants which have Relative Barrier Penetration Values of greater than 75 can be used along with the mild surfactant at low levels in the compositions of this invention, as long as their use does not significantly change the clinical skin mildness of the total cleansing composition.

Thus according to another aspect of the invention, there is provided a personal cleansing composition comprising:

- (a) from about 5% to about 50% by weight of a mixed surfactant system having a Relative Skin Barrier Penetration Value of less than about 75,

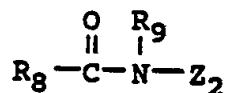
- (b) from about 3% to about 40% by weight of an insoluble, nonionic oil or wax or mixture of insoluble, nonionic oils or waxes, and
- (c) water,

wherein the weight ratio of total surfactant: nonionic oil or wax is in the range from about 10:1 to about 1:3, and wherein the composition is in the form of an oil-in-water emulsion having a viscosity (Brookfield RVT, Helipath, Spindle TB, 5 rmp, 25°C, 1min) in the range from 10,000 to 40,000 cps and a yield point of at least 50 dynes/cm² (Brookfield RVT, Spindle CP52, Plate Code A, 25°C).

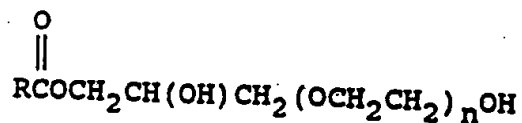
The compositions herein preferably also contain from about 0.1% to about 20%, more preferably from about 0.1% to about 10%, and especially from about 1% to about 8% of a nonionic or betaine surfactant. Preferred herein from the viewpoint of optimum lathering and mildness are nonionic surfactants selected from C₁₂-C₁₄ fatty acid mono- and diethanolamides; alkylpolysaccharides having the general formula (VI)



where Z is a moiety derived from glucose, fructose or galactose, R is C₈-C₁₈ alkyl or alkenyl, n is 2 or 3, t is from 0 to 10 and x is from about 1 to 10, preferably from about 1.5 to 4; polyhydroxy fatty acid amide surfactants having the general formula (VII)



where R₉ is H, C₁-C₄ hydrocarbyl, 2-hydroxyethyl, 2-hydroxypropyl or a mixture thereof, R₈ is C₅-C₃₁ hydrocarbyl and Z₂ is a polyhydroxyhydrocarbyl having a linear chain with at least 3 hydroxyls directly connected to said chain, or an alkoxylated derivative thereof; and polyethyleneglycol glyceryl fatty ester surfactants having the formula (IX)



wherein n is from about 5 to about 200, preferably from about 20 to about 100, more preferably from about 30 to about 85, and wherein R comprises an aliphatic radical having from about 5 to 19 carbon atoms, preferably from about 9 to 17 carbon atoms, more preferably from about 11 to 17 carbon atoms, most preferably from about 11 to 14 carbon atoms; and mixtures of said alkyl polysaccharide, amide or glyceryl fatty ester surfactants.

The preferred alkyl polysaccharides herein are alkylpolyglucosides having the formula VI wherein Z is a glucose residue, R is C₈-C₁₈ alkyl or alkenyl, t is from 0 to 10, preferably 0, n is 2 or 3, preferably 2, and x is from about 1.5 to 4. In the above, x and t are understood to be weight average values and saccharide substitution is preferably at the 1- position of the saccharide. In general terms, C₁₂-C₁₄ alkyl polysaccharides are preferred from the viewpoint of lathering and C₈-C₁₀ alkyl polysaccharides from the viewpoint of skin conditioning.

To prepare these compounds, a long chain alcohol (ROH) can be reacted with glucose, in the presence of an acid catalyst to form the desired glucoside. Alternatively, the alkylpolyglucosides can be prepared by a two step procedure in which a short chain alcohol (C₁₋₆) is reacted with glucose or a polyglucoside (x = 2 to 4) to yield a short chain alkyl glucoside (x = 1 to 4) which can in turn be reacted with a longer chain alcohol (ROH) to displace the short chain alcohol and obtain the desired alkylpolyglucoside. If this two step procedure is used, the short chain alkylglucoside content of the final alkylpolyglucoside material should be less than 50%, preferably less than 10%, more preferably less than 5%, most preferably 0% of the alkylpolyglucoside.

The amount of unreacted alcohol (the free fatty alcohol content) in the desired alkylpolysaccharide surfactant is preferably less than about 2%, more preferably less than about 0.5% by weight of the total of the alkyl polysaccharide plus unreacted alcohol. The amount of

alkylmonosaccharide is about 20% to about 70%, preferably 30% to 60%, more preferably 30% to 50% by weight of the total of the alkylpolysaccharide.

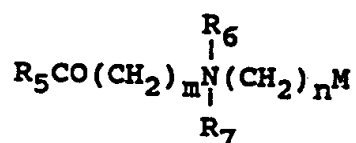
The preferred polyhydroxy fatty acid amide surfactants are those in which R_9 is C_{1-4} alkyl, preferably methyl, and R_8 is C_7-C_{19} alkyl or alkenyl, more preferably straight-chain C_9-C_{17} alkyl or alkenyl, or mixture thereof; and Z_2 is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxylated or propoxylated) thereof. Z_2 preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z_2 is a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z_2 . It should be understood that it is by no means intended to exclude other suitable raw materials. Z_2 preferably will be selected from the group consisting of - $CH_2(CHOH)_n-CH_2OH$, $-CH(CH_2OH)-(CHOH)_{n-1}-CH_2OH$, $-CH_2-(CHOH)_2(CHOR')(CHOH)-CH_2OH$, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide, and alkoxyated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly $-CH_2-(CHOH)_4-CH_2OH$.

The most preferred polyhydroxy fatty acid amide has the formula $R_8(CO)N(CH_3)CH_2(CHOH)_4CH_2OH$ wherein R_8 is a $C_{11}-C_{17}$ straight chain alkyl or alkenyl group.

Suitable glyceryl fatty ester surfactants include polyethyleneglycol derivatives of glyceryl cocoate, glyceryl caproate, glyceryl caprylate, glyceryl tallowate, glyceryl palmate, glyceryl stearate, glyceryl laurate, glyceryl oleate, glyceryl ricinoleate, and glyceryl fatty esters derived from triglycerides, such as palm oil, almond oil, and corn oil, preferably glyceryl tallowate and glyceryl cocoate.

Suitable surfactants of this class are commercially available from Sherex Chemical Co. (Dublin, Ohio, USA) under their Varonic LI line of surfactants. These include, for example, Varonic LI 48 (polyethylene glycol (n=80) glyceryl tallowate, alternatively referred to as PEG 80 glyceryl tallowate), Varonic LI 2 (PEG 28 glyceryl tallowate), Varonic LI 420 (PEG 200 glyceryl tallowate), and Varonic LI 63 and 67 (PEG 30 and PEG 80 glyceryl cocoates), and from Croda Inc. (New York, USA) under their Crovol line of materials, such as Crovol A-40 (PEG 20 almond glyceride), Crovol A-70 (PEG 60 almond glyceride), Crovol M-40 (PEG 20 maize glyceride), Crovol M-70 (PEG 60 maize glyceride), Crovol PK-40 (PEG 12 palm kernel glyceride), and Crovol PK-70 (PEG 45 palm kernel glyceride). Especially preferred are monotallowate and cocoate fatty ester derivatives of polyethylene glycol, or mixtures thereof, particularly materials such as PEG 82 glyceryl monotallowate and PEG 30 glyceryl cocoate, and mixtures thereof. Also especially preferred herein is PEG (6) capric/caprylic glyceride (Softigen 767).

Betaine surfactants suitable for inclusion in the composition of the invention include alkyl betaines of the formula $R_5R_6R_7N^+(CH_2)_nM$ (VII) and amido betaines of the formula (VIII)

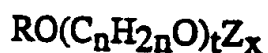


wherein R_5 is C_{12} - C_{22} alkyl or alkenyl, R_6 and R_7 are independently C_1 - C_3 alkyl, M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium, and n, m are each numbers from 1 to 4. Preferred betaines include cocoamidopropyldimethylcarboxymethyl betaine and laurylamidopropyldimethylcarboxymethyl betaine.

Of the above nonionic and betaine surfactants, highly preferred for use herein are the alkylpolysaccharides having the general formula VI, this being preferred from the viewpoint of providing optimum lathering, mildness, emolliency, rinsibility and stability characteristics. Thus,

according to another aspect of the invention, there is provided a personal cleansing composition comprising:

- (a) from about 5% to about 50% by weight of a mixed surfactant system which comprises
 - (i) from about 1% to about 20% by weight of anionic surfactant,
 - (ii) from about 1% to about 20% by weight of amphoteric surfactant, and
 - (iii) from about 0.1% to about 20% by weight of alkylpolysaccharide having the general formula (VI)



where Z is a moiety derived from glucose, fructose or galactose, R is C₈-C₁₈ alkyl or alkenyl, n is 2 or 3, t is from 0 to 10 and x is from about 1 to 10, preferably from about 1.5 to 4

- (b) from about 3% to about 40% of an insoluble, nonionic oil or wax or mixture of insoluble nonionic oils or waxes, and
- (c) water,

wherein the anionic surfactant and amphoteric surfactant together comprise from about 5% to about 30% by weight of the composition, the weight ratio of anionic surfactant:amphoteric surfactant is in the range from about 1:5 to about 20:1, the weight ratio of total surfactant: nonionic oil or wax is in the range from about 10:1 to about 1:3, and wherein the composition is in the form of an oil-in-water emulsion having a viscosity (Brookfield RVT, Helipath, Spindle TB, 5 rmp, 25°C, 1min) in the range from 10,000 to 40,000 cps and a yield point of at least 50 dynes/cm² (Brookfield RVT, Spindle CP52, Plate Code A, 25°C).

The compositions of the invention preferably also contain from about 0.5% to about 6%, preferably from about 1.5% to about 5% by weight of saturated or unsaturated acyl fatty acids having a weight average chain length of from 10 to 18, preferably from 12 to 16 carbon

atoms. Highly preferred are myristic saturated fatty acid and palm kernel unsaturated fatty acid. The fatty acid is valuable both from the viewpoint of providing emolliency benefits and also for controlling the viscosity and stability of the final composition. Highly preferred from the viewpoint of providing optimum viscosity and low temperature stability characteristics are compositions comprising the unsaturated fatty acids.

According to a further aspect of the invention therefore, there is provided a personal cleansing composition comprising:

- (a) from about 5% to about 50% by weight of a mixed surfactant system which comprises:
 - (i) from about 1% to about 20% by weight of composition of anionic surfactant, and
 - (ii) from about 1% to about 20% by weight of composition of amphoteric surfactant,
- (b) from about 3% to about 40% by weight of an insoluble, nonionic oil or wax or mixture of insoluble, nonionic oils or waxes;
- (c) from about 0.5% to about 8% by weight of unsaturated fatty acid, with weight average carbon chain length of from 10 to 18 carbon atoms; and
- (d) water,

wherein the anionic surfactant and amphoteric surfactant together comprise from about 5% to about 30% by weight of the composition, the weight ratio of anionic surfactant : amphoteric surfactant is in the range from about 1:5 to about 20:1, the weight ratio of total surfactant : nonionic oil or wax is in the range from about 10:1 to about 1:3, and wherein the composition is in the form of an oil-in-water emulsion having a viscosity (Brookfield RVT, Helipath, Spindle TB, 5rpm, 25°C, 1 min) in the range from 10,000 to 40,000 cps and a yield point of at least 50 dynes/cm² (Brookfield RVT, Spindle CP52, Plate Code A, 25°C).

The compositions of the invention preferably also contain a cationic or nonionic polymeric skin or hair conditioning agent at a level from about 0.01 % to about 5 %, preferably from about 0.04 % to about 2 % and especially from about 0.05 % to about 1 %. The polymer is found to be valuable for enhancing the creaminess and quality of the foam as well as providing a hair or skin conditioning utility.

Suitable polymers are high molecular weight materials (mass-average molecular weight determined, for instance, by light scattering, being generally from about 2,000 to about 3,000,000, preferably from about 5,000 to about 1,000,000).

Useful polymers are the cationic, nonionic, amphoteric, and anionic polymers useful in the cosmetic field. Preferred are cationic and nonionic polymers used in the cosmetic fields as hair or skin conditioning agents.

Representative classes of polymers include cationic and nonionic polysaccharides; cationic and nonionic homopolymers and copolymers derived from acrylic and/or methacrylic acid; cationic and nonionic cellulose resins; cationic copolymers of dimethyldiallylammonium chloride and acrylic acid; cationic homopolymers of dimethyldiallylammonium chloride; cationic polyalkylene and ethoxypolyalkylene imines; quaternized silicones, and mixtures thereof.

By way of exemplification, cationic polymers suitable for use herein include cationic guar gums such as hydroxypropyl trimethyl ammonium guar gum (d.s. of from 0.11 to 0.22) available commercially under the trade names Jaguar C-14-S(RTM) and Jaguar C-17(RTM) and also Jaguar C-16(RTM), which contains hydroxypropyl substituents (d.s. of from 0.8-1.1) in addition to the above-specified cationic groups, and quaternized cellulose ethers available commercially under the trade names Ucare Polymer JR and Celquat. Other suitable cationic polymers are homopolymers of dimethyldiallylammonium chloride available commercially under the trade name Merquat 100, copolymers of dimethyl aminoethylmethacrylate and acrylamide, copolymers of dimethyldiallylammonium chloride and acrylamide, available commercially under the trade names Merquat 550 and Merquat S,

quaternized vinyl pyrrolidone acrylate or methacrylate copolymers of amino alcohol available commercially under the trade name Gafquat, and polyalkyleneimines such as polyethylenimine and ethoxylated polyethylenimine.

Anionic polymers suitable herein include hydrophobically-modified cross-linked polymers of acrylic acid having amphipathic properties as marketed by B F Goodrich under the trade name Pemulen TRI and Pemulen TR2; and the carboxyvinyl polymers sold by B F Goodrich under the trade mark Carbopol and which consist of polymers of acrylic acid cross-linked with polyallyl sucrose or polyallyl pentaerythritol, for example, Carbopol 934, 940 and 950.

The viscosity of the final composition (Brookfield RVT, Spindle 5, 50 rpm, 25°C) is preferably at least about 1,000 cps, more preferably from about 2000 to about 10,000 cps, especially from about 5,000 to about 7,000 cps. Preferred compositions have non-Newtonian viscosity characteristics, however, with a viscosity (Brookfield RVT, Helipath, Spindle T-B, 5 rpm, 25°C, 1 min) in the range of from about 10,000 to about 40,000 cps, more preferably from about 20,000 to about 30,000 cps and a yield point (shear stress at zero shear rate) of at least 50 dynes/cm², preferably at least 100 dynes/cm² (Brookfield RVT, Spindle CP52, Plate Code A, 25°C). In highly preferred embodiments, the composition of the invention also display a shear stress versus temperature profile such that $(S_{45}-S_5)/S_5$ is less than about 0.4, preferably less than about 0.2, and more preferably less than about 0.1, where S_t is the shear stress in dynes/cm² at temperature t (°C) and at a shear rate of 500 sec⁻¹ (Brookfield RVT, Spindle CP52, Plate Code A).

It is a feature of the compositions of the invention that the particular surfactant mixtures employed therein display excellent lathering characteristics even in the presence of high levels of dispersed oil phase. Although the reasons for this are not fully understood, it is believed to reflect at least in part, the rheological properties of the compositions of the invention and in particular the rheological behaviour of the compositions as they are admixed with water during use.

The cleansing compositions can optionally include a hair or skin moisturizer which is soluble in the cleansing composition matrix. The preferred level of moisturizer is from about 0.5% to about 20% by weight. In preferred embodiments, the moisturizer is selected from:

1. water-soluble liquid polyols;
2. essential amino acid compounds found naturally occurring in the stratum corneum of the skin; and
3. water-soluble nonpolyol nonocclusives and mixtures thereof.

Some examples of more preferred nonocclusive moisturizers are glycerine, polyethylene glycol, propylene glycol, sorbitol, polyethylene glycol and propylene glycol ethers of methyl glucose (e.g. methyl glucam-20), sodium pyrrolidone carboxylic acid, lactic acid, urea, L-proline, guanidine, pyrrolidone, hydrolyzed protein and other collagen-derived proteins, aloe vera gel and acetamide MEA and mixtures thereof. Of the above, glycerine is highly preferred.

A number of additional optional materials can be added to the cleansing compositions. Such materials include proteins and polypeptides and derivatives thereof; water-soluble or solubilizable preservatives such as DMDM Hydantoin, Germall 115, methyl, ethyl, propyl and butyl esters of hydroxybenzoic acid, EDTA, Euxyl (RTM) K400, Bronopol (2-bromo-2-nitropropane-1,3-diol), sodium benzoate and 2-phenoxyethanol; other moisturizing agents such as hyaluronic acid, chitin, and starch-grafted sodium polyacrylates such as Sanwet (RTM) IM-1000, IM-1500 and IM-2500 available from Celanese Superabsorbent Materials, Portsmouth, VA, USA and described in US-A-4,076,663; solvents such as hexylene glycol and propylene glycol; low temperature phase modifiers such as ammonium ion sources (e.g. NH_4Cl); viscosity control agents such as magnesium sulfate and other electrolytes; colouring agents; pearlescers and opacifiers such as ethylene glycol distearate, TiO_2 and TiO_2 -coated mica; perfumes and perfume solubilizers etc. Water is also present at a level preferably of from about 45% to about 92% preferably at least about 60% by weight of the compositions herein.

The pH of the compositions is preferably from about 4 to about 8, more preferably from about 4.5 to about 6.5.

The invention is illustrated by the following non-limiting examples.

In the examples, all concentrations are on a 100% active basis and the abbreviations have the following designation:

Amphoteric 1	Empigen CDL 60 - an aqueous mixture of 23.5% cocoamphoacetate (the amphoteric of formula I and/or IV in which R_1 is coconut alkyl, R_2 is H, and Z is CO_2Na) and 1.35% cocoamphodiacetate (the amphoteric of formula I and/or IV in which R_1 is coconut alkyl, R_2 is $\text{CH}_2\text{CO}_2\text{Na}$ and Z is CO_2Na).
Amphoteric 2	Sodium N-lauryl-beta-amino-propionate.
Anionic 1	Sodium laureth-2 sulfate
Anionic 2	Magnesium sodium laureth 3.6 sulfate
APG	Alkylpolysaccharide of formula VI in which R is C_8 - C_{10} alkyl, t is 0, Z is a glucose residue and x is about 1.5.
GA	Polyhydroxy fatty acid amide of formula VII in which R_8 is C_{11} - C_{17} alkyl, R_9 is methyl, and Z_2 is $\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}$
DEA	Coconut diethanolamide
MEA	Coconut monoethanolamide
Betaine	Cocoamidopropyldimethylcarboxymethyl betaine

Polymer 1	Merquat 550 - Copolymer of acrylamide and dimethyldiallyl ammonium chloride, m.wt. 2.5×10^6 (8% solution)
Polymer 2	Polymer JR-400 - hydroxyethylcellulose reacted with epichlorohydrin and quaternized with trimethylamine, m.wt. 4×10^6
MA	Myristic Acid
PKA	Palm Kernel Acid
Preservative	DMDM Hydantoin
Pearlescer	Ethyleneglycoldistearate/emulsifier mixture
Oil	Soyabean oil
Softigen 767	PEG(6) caprylic/capryl glycerate
Mg	Magnesium sulfate heptahydrate

Examples I to VII

The following are personal cleansing compositions in the form of shower foam products and which are representative of the present invention:

	I	II	III	IV	V	VI	VII	VIII
Amphoteric 1	7.5	3.0	5.0	5.0	2.5	5.0	5.0	5.0
Amphoteric 2	-	5.0	3.0	-	5.0	-	-	-
Anionic 1	2.5	-	6.0	4.0	7.5	10.0	10.0	10.0
Anionic 2	5.0	9.0	4.0	6.0	-	-	-	-
APG	2.5	1.0	2.0	-	-	2.5	-	-
GA	-	1.0	-	2.0	2.0	-	2.5	2.5
DEA	3.0	1.0	-	2.0	1.0	3.0	-	3.0
MEA	-	-	-	-	-	-	3.0	-
Betaine	-	2.0	2.0	1.0	2.5	2.5	-	2.5
Polymer 1	-	0.1	0.2	-	0.1	0.2	-	0.2
Polymer 2	0.2	0.1	-	0.2	0.1	-	0.2	-
Softigen 767	-	-	-	-	-	2.0	1.0	2.0
MA	4.0	2.0	1.5	1.0	2.0	2.0	2.0	-
PKA	-	-	-	-	-	-	-	2.0
Oil	8.0	12.0	9.0	12.0	8.0	10.0	11.0	10.0
Preservative	0.15	0.15	0.15	0.15	0.15	0.2	0.2	0.2

Compositions I to VII are prepared by forming a surfactant phase A containing a portion of the water, the anionic and amphoteric surfactants and the remaining water-soluble, oil-insoluble ingredients, forming an oil phase B containing the MA, DEA, Softigen and oil, admixing B with A at about 40°-70°C, cooling to ambient temperature then adding the remaining water, preservative and water. The average particle size of the emulsion droplets is about 5 micron. (Malvern Series 2600 laser diffraction). The compositions have a viscosity (Brookfield RVT, Helipath, Spindle TB, 5 rmp, 25°C, 1min) in the range from 10,000 to 40,000 cps and a yield point of at least 50 dynes/cm² (Brookfield RVT, Spindle CP52, Plate Code A, 25°).

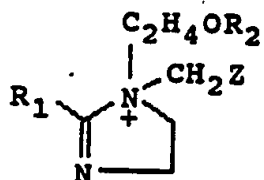
The products provide excellent in-use and efficacy benefits including cleansing, lathering, mildness and skin conditioning (hydration, suppleness etc.), rinsibility and stability.

CLAIMS

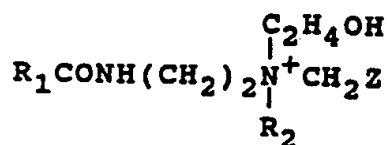
1. A personal cleansing composition comprising:
 - (a) from about 5% to about 50% by weight of a mixed surfactant system which comprises:
 - (i) from about 1% to about 20% by weight of composition of anionic surfactant, and
 - (ii) from about 1% to about 20% by weight of composition of amphoteric surfactant,
 - (b) from about 3% to about 40% by weight of an insoluble, nonionic oil or wax or mixture of insoluble, nonionic oils or waxes, and
 - (c) water,

wherein the anionic surfactant and amphoteric surfactant together comprise from about 5% to about 30% by weight of the composition, the weight ratio of anionic surfactant:amphoteric surfactant is in the range from about 1:5 to about 20:1, the weight ratio of total surfactant: nonionic oil or wax is in the range from about 10:1 to about 1:3, and wherein the composition is in the form of an oil-in-water emulsion having a viscosity (Brookfield RVT, Helipath, Spindle TB, 5 rmp, 25°C, 1min) in the range from 10,000 to 40,000 cps and a yield point of at least 50 dynes/cm² (Brookfield RVT, Spindle CP52, Plate Code A, 25°), and wherein are excluded personal cleansing compositions which comprise an adduct prepared from vegetable oils containing non-conjugated polyunsaturated fatty acid esters which are conjugated and elaidinized and then modified via Diels - Alder addition with a member of the group consisting of acrylic acid, fumaric acid and maleic anhydride.

2. A composition according to Claim 1 wherein the anionic surfactant is selected from ethoxylated alkyl sulfates, alkyl glyceryl ether sulfonates, methyl acyl taurates, fatty acyl glycinate, N-acyl glutamates, acyl isethionates, alkyl sulfosuccinates, alpha-sulfonated fatty acids, their salts and/or their esters, alkyl phosphate esters, ethoxylated alkyl phosphate esters, acyl sarcosinates and fatty acid/protein condensates, and mixtures thereof.
3. A composition according to Claim 1 or 2 comprising from about 2% to about 15%, preferably from about 3% to about 12% by weight of each of the anionic surfactant and the amphoteric surfactant.
4. A composition according to any of Claims 1 to 3 wherein the anionic surfactant comprises an ethoxylated C₈-C₂₂ alkyl sulfate.
5. A composition according to any of Claims 1 to 4 wherein the amphoteric surfactant is selected from:
 - (a) imidazolinium derivatives of formula (II)



wherein R₁ is C₇-C₂₂ alkyl or alkenyl, R₂ is hydrogen or CH₂Z, each Z is independently CO₂M or CH₂CO₂M, and M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium; and/or ammonium derivatives of formula (III)



wherein R_1 , R_2 and Z are as defined above:

- (b) aminoalkanoates of formula (IV)



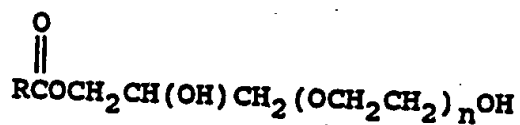
and iminodialkanoates of formula (V)



wherein n and m are numbers from 1 to 4, and R_1 and M are independently selected from the groups specified in (a) above; and

- (c) mixtures thereof.
6. A composition according to Claim 5 wherein the amphoteric is selected from the imidazolinium derivatives of formula II and/or ammonium derivatives of formula III.
 7. A composition according to any of Claims 1 to 6 wherein the weight ratio of anionic surfactant:amphoteric surfactant is in the range from about 1:2 to about 5:1.
 8. A composition according to Claim 7 wherever the weight ratio of anionic surfactant:amphoteric surfactant is in the range from about 1:1 to about 2:1.
 9. A composition according to any of Claims 1 to 8 wherein the anionic surfactant and amphoteric surfactant together comprise from about 8% to about 25%, preferably from about 10% to about 20% by weight of the composition.

10. A composition according to any of Claims 1 to 9 additionally comprising from about 0.1% to about 20%, preferably from about 0.1% to about 10% by weight of nonionic or betaine surfactant or mixture thereof.
11. A composition according to Claim 10 wherein the nonionic surfactant is selected from alkyl polysaccharides having the general formula $RO(C_nH_2O)_tZ_x$ where Z is a moiety derived from glucose, fructose or galactose, R is C₈-18 alkyl or alkenyl, n is 2 or 3, t is from 0 to 10 and x is from 1.5 to 4; polyhydroxy fatty acid amide surfactants having the formula $R_g(CO)N(R_9)Z_2$ wherein R₉ is H, C₁-C₄ hydrocarbyl, 2-hydroxyethyl, 2-hydroxypropyl or a mixture thereof, R_g is C₅-C₃₁ hydrocarbyl and Z₂ is a polyhydroxyhydrocarbyl having a linear chain with at least 3 hydroxyls directly connected to said chain, or an alkoxyated derivative thereof; polyethyleneglycol glyceryl fatty ester surfactants having the formula (IX)



wherein n is from about 5 to about 200, preferably from about 20 to about 100, more preferably from about 30 to about 85, and wherein R comprises an aliphatic radical having from about 5 to 19 carbon atoms, preferably from about 9 to 17 carbon atoms, more preferably from about 11 to 17 carbon atoms, most preferably from about 11 to 14 carbon atoms; and mixtures of said amide or glyceryl fatty ester surfactants

12. A composition according to any of Claims 1 to 11 comprising from about 5% to about 20%, preferably from about 8% to about 15% by weight of the nonionic oil or wax or mixture thereof.
13. A composition according to any of Claims 1 to 12 additionally comprising from about 0.5% to about 6%, preferably from about 1.5% to about 5% by weight of a saturated or unsaturated fatty acid

having a weight-average chain length of from 10 to 18, preferably 12 to 16 carbon atoms.

14. A composition according to any of Claims 1 to 13 additionally comprising from 0.01% to 5%, preferably from about 0.04% to about 2% and more preferably from 0.05% to 1% of a cationic or nonionic polymeric skin or hair conditioning agent, selected from cationic and nonionic polysaccharides; cationic and nonionic homopolymers and copolymers derived from acrylic and/or methacrylic acid, cationic and nonionic cellulose resins; cationic copolymers of dimethyldiallylammonium chloride and acrylic acid; cationic homopolymers of dimethyldiallylammonium chloride; cationic polyalkylene and ethoxypolyalkylene imines; quaternized silicones, and mixtures thereof.
15. A composition according to any of Claims 1 to 14 additionally comprising moisturiser selected from glycerin, polyethylene glycol, propylene glycol, sorbitol, polyethylene glycol and polypropylene glycol ethers of methyl glucose, polyethylene glycol and polypropylene glycol ethers of lanolin alcohol, PEG(6) caprylic/capryl glycerate, sodium pyrrolidone carboxylic acid, lactic acid, L-proline and mixtures thereof.
16. A composition according to any of Claims 1 to 15 wherein the anionic surfactant comprises at least 50%, preferably at least 75% thereof of ethoxylated C₈-C₂₂ alkyl sulfate and wherein the surfactant counterions are selected from magnesium and mixtures of magnesium with one or more counterions selected from alkalimetal, ammonium and alkanolammonium.
17. A composition according to any one of Claims 1 to 16 wherein the weight ratio of total surfactant:nonionic oil or wax is in the range from about 5:1 to about 1:2, preferably from about 2:1 to about 1:1.

18. A personal cleansing composition comprising:
- (a) from about 5% to about 50% by weight of a mixed surfactant system which comprises:
 - (i) from about 1% to about 20% by weight of composition of anionic surfactant, and
 - (ii) from about 1% to about 20% by weight of composition of amphoteric surfactant,
 - (b) from about 3% to about 40% by weight of an insoluble, nonionic oil or wax or mixture of insoluble, nonionic oils or waxes;
 - (c) from about 0.5% to about 8% by weight of unsaturated fatty acid with weight average carbon chain length of from 10 to 18 carbon atoms; and
 - (d) water,

wherein the anionic surfactant and amphoteric surfactant together comprise from about 5% to about 30% by weight of the composition, the weight ratio of anionic surfactant : amphoteric surfactant is in the range from about 1:5 to about 20:1, the weight ratio of total surfactant : nonionic oil or wax is in the range from about 10:1 to about 1:3, and wherein the composition is in the form of an oil-in-water emulsion having a viscosity (Brookfield RVT, Helipath, Spindle TB, 5rpm, 25°C, 1 min) in the range from 10,000 to 40,000 cps and a yield point of at least 50 dynes/cm² (Brookfield RVT, Spindle CP52, Plate Code A, 25°C).

INTERNATIONAL SEARCH REPORT

PCT/US93/02411

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C11D 1/94,3/16

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. :

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US, A, 5,002,680 (SCHMIDT ET AL.) 26 March 1991, See abstract; column 3, lines 24-33 and examples.	<u>1-3</u> 18
Y	US, A, 4,812,253 (SMALL ET AL.) 14 March 1989, See abstract; column 7, lines 30-40 and claim 1.	1-3 & 18
Y,P	US, A, 5,186,857 (RAMIREZ ET AL.) 16 February 1993, See abstract, column 3, lines 9-43 and example 22.	1-3
Y,P	US,A, 5,188,756 (BAKER ET AL.) 23 February 1993, See example 2 and column 2, lines 24-39.	1-3 & 18

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be part of particular relevance	X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	A*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 22 APRIL 1993	Date of mailing of international search report JUL 1993
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	Authorized officer for BRADLEY A. SWOPE Telephone No. (703) 308-2521

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/02411

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	US, A, 5,132,037 (GREENE ET AL.) 21 July 1992, See abstract and column 3, lines 13-16.	1-3 & 18
X Y	US, A, 3,829,563 (BARRY ET AL.) 13 August 1974, See abstract; column 4, lines 1-29 and examples.	1-3 18
Y	US, A, 5,085,857 (REID ET AL.) 04 February 1992, See abstract and examples.	1-3 & 18
A	US, A, 4,026,825 (STEEN ET AL.) 31 May 1977, See abstract.	1-3 & 18

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US93/02411

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

252/542,546,551,554,549,557,173,174.15,174.16, DIG. 5, DIG. 14; 424/70